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POLAROGRAPHIC STUDIES ON MIXED LIGAND COMPLEXES OF Cd(II) WITH ACETYLTHIOUREA AND CHLORIDE ION IN AQUEOUS SOLUTION**

The changes in polarograms obtained in Cd(II)-acetylthiourea chloride ion system were examined. The results were analised in terms of successively formed single and mixed ligand complexes of Cd(II) with acetylthiourea (AcTU) and chloride ion, their composition and overall free energy (ΔG), entalphy (ΔH), entropy (ΔS) changes for reaction: $Cd^{2+} + jCl^- + iAcTU \rightleftharpoons CdCl_jAcTU_i^{2-j}$.

In our previous study [1] concerning mixed complexes of Cd(II) with AcTU and Br^- in water-alcohol solutions we have shown the formation of the following complexes: $CdAcTUBr^+$, $CdAcTUBr_2$, $CdAcTU_2Br_2$ and $CdAcTU_3Br^+$. In this paper we present the results of polarographic investigations of Cd-AcTU-Cl^- system obtained at different temperatures, aimed at finding the composition, stability constants and overall ΔG, ΔH and ΔS changes of single and mixed ligand complexes formed within this system.

EXPERIMENTAL

All chemicals were of reagent grade. The ionic strengh was kept constant (μ = 1.0) by adding amouns of KNO_3. KNO_3 was chosen because NO_3^- anions show low ability to form complexes [2] and therefore they do not disturb the formation of complexes of Cd(II)

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with the investigated ligands. The concentration of Cd(II) ions ($c_{Cd} = 2 \times 10^{-4}$ mol · dm^{-3}) and Cl^- ions were constant during measurements, while the concentration of AcTU was changed from 0.00 to 0.45 mol · dm^{-3}. Series of measurements were carried out for several constant concentrations of Cl^- (c_{Cl}): 0.10, 0.15, 0.20 and 0.30 mol · dm^{-3} at the following temperatures: 293, 298, 303, 308, 313 K. A OH-104 Radelkis polarograph was used. A saturated calomel electrode was used as a reference one and a mercury dropping electrode was the indicator electrode. The potential of mercury dropping electrode (E_{MDE}) was continuously controlled by the third electrode in the form of cylinder of platinum gause, 1.5×10^{-2} m in the diameter and 2×10^{-2} m in length. Purified nitrogen was used to remove oxygen from the solutions under investigation.

RESULTS AND DISCUSSION

The polarographic reduction process in the investigated system Cd(II)-AcTU-Cl^--H_2O is reversible and controlled by diffusion. The slopes of linear plots of log i/i_g-i vs. E_{MDE} are 0.029 V per a logarithm unit and the plots of i_g vs. $h^{1/2}_{corr}$ are linear. Tables 1-4 show the values of $E_{1/2}$ obtained graphically and those of i_g read polarograms. It following from these data that $E_{1/2}$ shifts towards negative values with increasing the concentration of AcTU at constant concentrations of Cd^{2+} and Cl^-.

Table 1

Values $E_{1/2}$, i_g, $F_{00}(X, Y)$ obtained from polarographic measurements

$C_{Cd} = 2 \times 10^{-4}$ mol/dm^3; $C_{Cl} = 0.3$ mol/dm^3; $\mu = 1$ mol/dm^3 (KNO_3); T = 298 K

$C_{Ac}TU$ (mol/dm^3)	$-E_{1/2}$ (V)	$i_g \times 10^6$ (A)	$F_{00}(X, Y)$
1	2	3	4
0.000	0.633	8.20	-
0.010	0.682	8.18	45.3
0.017	0.683	8.17	62.0

Table 1 (contd)

1	2	3	4
0.058	0.706	8.11	287
0.105	0.719	8.09	841
0.160	0.730	8.04	1 950
0.210	0.733	8.01	3 440
0.268	0.744	7.89	5 840
0.299	0.747	7.67	7 460
0.313	0.747	7.25	8 270
0.337	0.749	7.23	9 790
0.375	0.753	7.20	12 500
0.420	0.756	7.18	16 400
0.450	0.758	7.18	19 300

Table 2

Values $E_{1/2}$, i_g, $F_{00}(X, Y)$ obtained from polarographic measurements
$C_{Cd} = 2 \times 10^{-4}$ mol/dm^3; $C_{Cl} = 0.15$ mol/dm^3, $\mu = 1$ mol/dm^3 (KNO_3);
$T = 303$ K

C_{AcTU} [mol/dm^3]	$-E_{1/2}$ [V]	$i_g \times 10^6$ [A]	$F_{00}(X, Y)$
0.000	0.588	8.59	-
0.005	0.608	8.58	4.71
0.011	0.614	8.57	7.47
0.058	0.642	8.55	61.4
0.115	0.658	8.54	220
0.205	0.674	8.52	763
0.250	0.681	8.50	1 210
0.325	0.689	8.47	2 320
0.390	0.695	8.40	3 730
0.404	0.696	8.35	4 100
0.430	0.698	8.34	4 800
0.449	0.700	8.08	5 500

Table 3

Values $E_{1/2}$, i_g, $F_{00}(X, Y)$ obtained from polarographic measurements
$C_{Cd} = 2 \times 10^{-4}$ mol/dm^3; $C_{Cl} = 0.3$ mol/dm^3; $\mu = 1$ mol/dm^3 (KNO_3);
$T = 308$ K

C_{AcTU} (mol/dm^3)	$-E_{1/2}$ (V)	$i_g \times 10^6$ (A)	$F_{00}(X, Y)$
0.000	0.629	8.16	-
0.008	0.674	8.15	29.2
0.014	0.677	8.13	39.0
0.095	0.707	8.04	373
0.155	0.719	7.98	908
0.200	0.726	7.95	1 500
0.228	0.729	7.91	1 970
0.285	0.735	7.83	3 180
0.310	0.738	7.75	3 830
0.366	0.743	7.74	5 590
0.399	0.745	7.72	6 830
0.420	0.747	7.73	7 720
0.438	0.748	7.42	8 540
0.450	0.749	7.40	9 120

Table 4

Values $E_{1/2}$, i_g, $F_{00}(X, Y)$ obtained from polarographic measurements
$C_{Cd} = 2 \times 10^{-4}$ mol/dm^3; $C_{Cl} = 0.2$ mol/dm^3; $\mu = 1$ mol/dm^3 (KNO_3);
$T = 313$ K

C_{AcTU} (mol/dm^3)	$-E_{1/2}$ (V)	$i_g \times 10^6$ (A)	$F_{00}(X, Y)$
1	2	3	4
0.000	0.604	8.53	-
0.006	0.638	8.52	12.4
0.085	0.669	8.50	126
0.100	0.673	8.49	163
0.150	0.682	8.41	332

Table 4 (contd)

1	2	3	4
0.198	0.689	8.37	571
0.231	0.694	8.35	790
0.265	0.698	8.33	1 060
0.305	0.702	8.19	1 500
0.359	0.707	8.03	2 160
0.398	0.710	7.98	2 790
0.421	0.712	7.95	3 230
0.445	0.714	7.90	3 720

Hence, one can assume [3, 4] that in the investigated system takes place the formation of mixed ligand complexes of Cd(II) with AcTU and Cl^- according to the following reaction:

$$Cd(H_2O)_6^{2+} + iAcTU + jCl^- \rightleftharpoons Cd(AcTU)_i(Cl^-)_j(H_2O)_{6-i-j}{}^{2-j} + (i + j)H_2O \quad (1)$$

The stability of mixed ligand complexes is described by a constant of the formation equilibrium (stability constant), $\beta_{i,j}$ [5]. One of the methods for the determination of stability constant of mixed ligand complexes consists in the addition of two ligands X and Y over a wide concentration range of each of them.

The stability constant of mixed complex β_{ij} is associated with concentrations of complex $[MX_iY_j]$, free metal ions [M] and free ligands [X] and [Y]. The results were interpreted according the procedure describe in the paper [4]. For mathematical treatment of data in polarography the function of Leden F_{00} (X, Y) [4] is used (2):

$$F_{00}(X,Y) = \sum_{i=0}^{N-j} \cdot \sum_{j=0}^{N-i} \beta_{ij} \; [X]^i[Y]^j \quad (2)$$

This function is calculated from eq. (3) when the values of $E_{1/2}$ and of the limiting diffusion current i_g are known:

$$F_{00}(X,\ Y) = \exp \frac{nF}{RT}\left[(E_{1/2})_M - (E_{1/2})_K\right] + \ln \frac{i_{gK}}{i_{gK}} \qquad (3)$$

where: M concerns metal ion and K-complex.

Function $f_{00}(X,\ Y)$ for the investigated system can be described by eg. (4):

$$\begin{aligned} F_{00}(X,\ Y) = &\left\{\beta_{00} + \beta_{01}[Cl^-] + \beta_{02}[Cl^-]^2 + \beta_{03}[Cl^-]^3 + \beta_{04}[Cl^-]^4\right\} + \\ &+ \left\{\beta_{10} + \beta_{11}[Cl^-] + \beta_{12}[Cl^-]^2 + \beta_{13}[Cl^-]^3\right\}[AcTU] + \\ &+ \left\{\beta_{20} + \beta_{21}[Cl^-] + \beta_{22}[Cl^-]^2\right\}[AcTU]^2 + \\ &+ \left\{\beta_{30} + \beta_{31}[Cl^-]\right\}[AcTU]^3 + \left\{\beta_{40}\right\}[AcTU]^4 \qquad (4a) \end{aligned}$$

$$\begin{aligned} F_{00}(X,\ Y) = &F'_0 + F'_1\ [AcTU] + F'_2\ [AcTU]^2 + F'_3\ [AcTU]^3 + \\ &+ F'_4\ [AcTU]^4 \qquad (4b) \end{aligned}$$

The values of $F_{00}(X,\ Y)$ were calculated from the experimental data (Tab. 1-4). The values of F'_0, F'_1, F'_2, F'_3 and F'_4 were obtained by linear extrapolation (Fig. 1-3) of $F_{00}(X,\ Y)$, $F_{10}(X,\ Y)$, $F_{20}(X,\ Y)$, $F_{30}(X,\ Y)$ and $F_{40}(X,\ Y)$ described with eq. (5) at $c_{AcTU} \to 0$:

$$F_{j0}(X,\ Y) = \frac{F_{j-1,0}(X,\ Y) - F_j}{[AcTU]} \qquad (5)$$

where: $[AcTU] \simeq c_{AcTU}$.

The results (Tab. 1-4 and Fig. 1-4) are indicative of the formation of complexes in the system $Cd(II)$-AcTU-Cl^--H_2O. These complexes have the following compositions: $Cd^{2+} : Cl^- : AcTU = 1 : 1 : 1$, $1 : 1 : 2$, $1 : 1 : 3$, $1 : 2 : 1$ and $1 : 2 : 2$. The stability constants for these complexes were found from eq. (4). The values of log β are given in Tab. 5. The Fig. 6 shows the distribution diagram of complexes formed in the system $Cd(II)$-AcTU-Cl^- prepared according to the description given by Marcus [5] using the

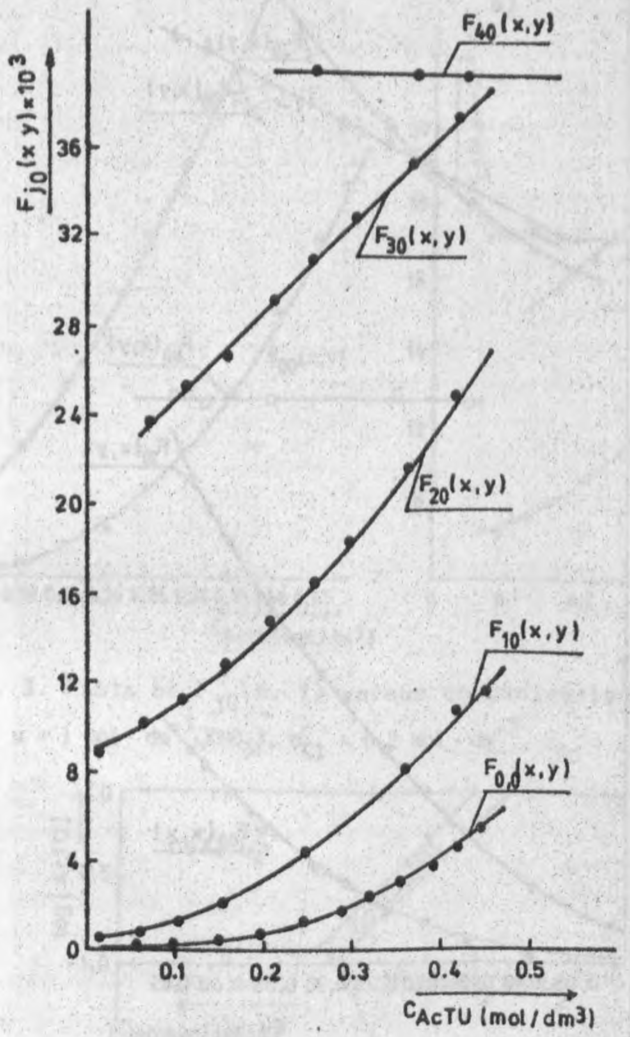

Fig. 1. Plots of $F_{j0}(X, Y)$ versus concentrations of AcTU $T = 298$ K, $\mu = 1\ \mathrm{mol \cdot dm^{-3}}$ (KNO_3), $c_{Cl} = 0.1\ \mathrm{mol \cdot dm^{-3}}$, $c_{Cd} = 2 \cdot 10^{-4}\ \mathrm{mol \cdot dm^{-3}}$

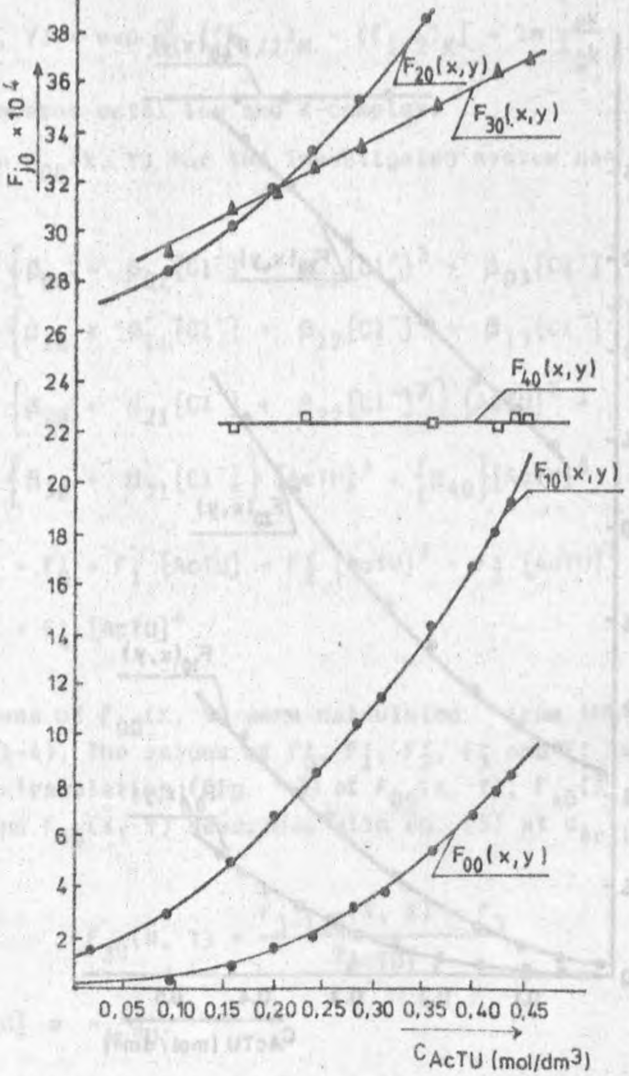

Fig. 2. Plots of $F_{j0}(X, Y)$ versus concentrations of AcTU
T = 308 K, $\mu = 1\ \mathrm{mol \cdot dm^{-3}}$ (KNO_3), $c_{Cl} = 0.3\ \mathrm{mol \cdot dm^{-3}}$, $c_{Cd} = 2 \cdot 10^{-4}\ \mathrm{mol \cdot dm^{-3}}$

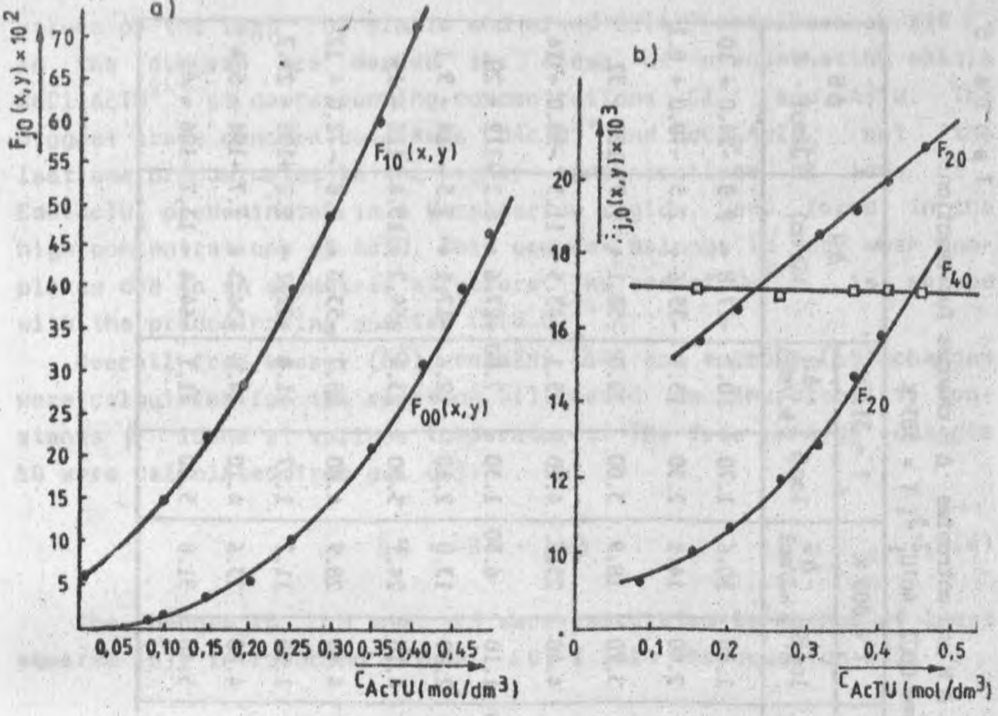

Fig. 3. Plots of $F_{j0}(X, Y)$ versus concentration AcTU
$T = 313$ K, $\mu = 1\ \mathrm{mol \cdot dm^{-3}}$ (KNO_3), $c_{Cl} = 0.2\ \mathrm{mol \cdot dm^{-3}}$, $c_{Cd} = 2 \cdot 10^{-4}\ \mathrm{mol \cdot dm^{-3}}$

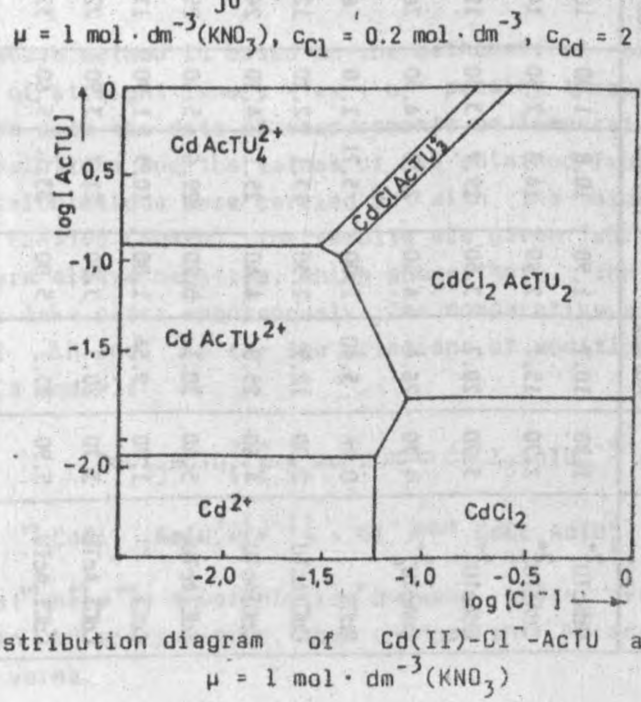

Fig. 4. Distribution diagram of Cd(II)-Cl^--AcTU at $T = 298$ K, $\mu = 1\ \mathrm{mol \cdot dm^{-3}}$ (KNO_3)

Table 5

Values overall free energies Δ G, enthalpies Δ H and entropies Δ S changes for reaction:
$Cd^{2+} + jCl^{-} + i\ AcTU \rightleftharpoons CdCl_{j}\ AcTU_{i}^{2-j}$; T = 303 K

Complex composition	T = 293 K		T = 298 K		T = 303 K		T = 308 K		T = 313 K		ΔH	ΔS
	logβ	-ΔG kJ/mol	logβ	-ΔG kJ/mol	logβ	-ΔG kJ/mol	logβ	-ΔG kJ/mol	logβ	-ΔG kJ/mol	kJ/mol	J/mol · K
$CdAcTU^{2+}$	1.90	10.7	1.90	10.8	1.80	10.4	1.80	10.6	1.70	10.2	-17.8 + 8.8	-24.0 + 10
$CdAcTU_2^{2+}$	2.70	15.1	2.60	14.8	2.50	14.5	2.40	14.1	2.30	13.7	-35.6 + 2.5	-70.0 + 8.1
$CdAcTU_3^{2+}$	3.70	20.7	3.50	19.9	3.30	19.1	3.20	18.9	3.00	18.0	-58.1 + 9.9	-128 + 32
$CdAcTU_4^{2+}$	4.70	26.4	4.60	26.2	4.50	26.0	4.40	25.9	4.20	25.1	-43.5 + 11.3	-58.0 + 14
$CdCl^{+}$	0.96	5.40	1.00	5.71	1.10	6.40	1.10	6.50	1.30	7.80	+27.6 + 6.2	+112 + 20
$CdClAcTU^{+}$	2.30	12.9	2.30	13.1	2.20	12.7	2.20	13.0	2.10	12.6	-17.1 + 7.5	-14 + 9.1
$CdClAcTU_2^{+}$	4.60	25.8	4.40	25.1	4.20	24.3	4.10	24.1	3.90	23.4	-59.7 + 15.4	-116 + 19
$CdClAcTU_3^{+}$	5.40	30.3	5.20	29.6	5.10	29.6	4.90	28.9	4.80	28.7	-53.0 + 9.8	-78.0 + 12
$CdCl_2$	1.70	9.54	1.80	10.3	1.90	11.0	1.90	11.2	1.97	11.8	+22.1 + 9.2	+108 + 29.7
$CdCl_2AcTU$	3.70	20.7	3.80	21.7	3.90	22.6	4.00	23.6	4.10	24.6	+36.1 + 1.7	+194 + 5.4
$CdCl_2AcTU_2$	5.90	33.1	5.80	33.1	5.60	32.5	5.40	31.8	5.20	31.1	-64.4 + 13,2	-106 + 43

values of the logβ of simple and mixed Cd(II) complexes at 298 K. In the diagram are marked the areas of predominating specis $CdCl_jAcTU^{2-j}$ at corresponding concentrations Cl^- and AcTU. The biggest areas concern complexes $CdAcTM^{2+}$ and $CdCl_2AcTU_2$ but the last one predominates in the higher concentrations of ions Cl^-. $CdClAcTU_3^+$ predominates in a very narrow region, and forms in the high concentrations of AcTU. This complex belongs to very weak complexes due to an asymetric structure. The are of Cd^{2+} is marked with the predominating species $Cd(H_2O)_6^{2+}$.

Overall free energy (ΔG), entalpy (ΔH) and entropy (ΔS) changes were calculated for the reaction (1) based on the stability constants β found at various temperatures. The free energy changes ΔG were calculated from eq. (6):

$$\Delta G = -RT \cdot \ln\beta \tag{6}$$

The changes in ΔH and ΔS were calculated by method of least squares [6], introducing values ΔG, T into the equation (7):

$$\Delta G = \Delta H - T \cdot \Delta S \tag{7}$$

The above method is based on the mathematical analysis of the equation of straight line y = ax + b passing through a number of points. We used the data of measurements on temperature T of inwestigated solutions and the values of ΔG obtained from equation (6).

The calculations were carried out with the aid a Scientific Computer EL-5500 (Sharp). The results are given Tab. 5. The changes in ΔG are always negative, which shows that the complexation processes take place spontanously. The comparative analysis of the values of ΔH and ΔS for the relations of addition of subsequent ligands (8 and 9):

$$CdCl_jAcTU_{i-1}^{2-j} + AcTU \rightleftharpoons CdCl_jAcTU_i^{2-j} \tag{8}$$

$$CdCl_{j-1}AcTU_i^{2-(j-1)} + Cl^- \rightleftharpoons CdCl_jAcTU_i^{2-j} \tag{9}$$

shows that there is a correlation between these values. If the changes in ΔH are positive, then changes in ΔS are also positive and vice versa.

Considering the values of ΔS of the formation of subsequent complexes $CdAcTU^{2+}$ according to reactions (10-13):

$$Cd^{2+} + AcTU \rightleftarrows CdAcTU^{2+} \qquad (\Delta S_1 = -24{,}0) \qquad (10)$$

$$CdAcTU^{2+} + AcTU \rightleftarrows CdAcTU_2^{2+} \qquad (\Delta S_2 = -70.0 + 24{,}0 = -46{,}0) \qquad (11)$$

$$CdAcTU_2^{2+} + AcTU \rightleftarrows CdAcTU_3^{2+} \qquad (\Delta S_3 = -128 + 70{,}0 = -58{,}0) \qquad (12)$$

$$CdAcTU_3^{2+} + AcTU \rightleftarrows CdAcTU_4^{2+} \qquad (\Delta S_4 = -58{,}0 + 128 = +70{,}0) \qquad (13)$$

where the values of ΔS is in J/mol · K.

One can state the values of ΔS_n changes in the following way:

$$0 > \Delta S_1 > \Delta S_2 > \Delta S_3 < \Delta S_4 > 0.$$

A distinct increase in the entropy of the addition of the fourth AcTU molecule (eq. 13) is observed. The changes in enthalpy are the same. Similar changes in ΔH and ΔS are observed in reaction (8) when $p = 1$ and the third AcTU molecule is added to form $CdClAcTU_3^+$. These positive changes in the values of ΔS and ΔH can be brought about by the change in coordination from octahedral to tetrahedral one in the complex containing four ligands. Similar changes in the values of ΔS and ΔH were found also in $CdCl_jMeTU_i^{2-j}$ [8].

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POLAROGRAFICZNE BADANIA KOMPLEKSÓW MIESZANYCH Cd(II) Z ACETYLOTIOMOCZNIKIEM I JONEM CHLORKOWYM W ROZTWORZE WODNYM

Prześledzono zmiany na polarogramach otrzymanych w układzie: Cd(II)-acetylotiomocznik-jon chlorkowy-H_2O. Wyniki poddano analizie z punktu widzenia liczby kolejno powstających kompleksów prostych i mieszanych Cd(II) z acetylotiomocznikiem i jonem Cl^-, ich składu, trwałości oraz ogólnych zmian funkcji termodynamicznych ΔG, ΔH i ΔS reakcji tworzenia tych kompleksów: $Cd^{2+} + jCl^- + iAcTM \rightleftarrows CdCl_jAcTM_i^{2-j}$.